Dept of Physics (History)

OAR:
The Basic Research Agency
of The United States Air Force

AF OFFICE OF SCIENTIFIC RESEARCH / AF CAMBRIDGE RESEARCH LABORATORIES / AERONAUTICAL RESEARCH LABORATORY / EUROPEAN OFFICE, OAR

NO. 7 4 JUNE 1962

Basic Research on the Morphology of High Polymers

DR. W. E. GIBBS, Materials and Processes Directorate, Aeronautical Systems Division (AFSC)

It is now generally realized that the mechanical properties of polymer systems may frequently be more affected by morphological properties (by crystallinity for example) than by primary molecular parameters such as molecular weight or chain branching. The morphology is thus of obvious importance in determining the behavior of these polymers. However, the inter-relations between molecular structure, processing history, and the resulting morphology are exceedingly complex, and their understanding is still at a very rudimentary level. While it has long been customary to speak of crystalline and amorphous polymers, it has not always been recognized that (1) the concepts of crystalline and amorphous regions may be inadequate in many cases and (2) there may exist diffuse types of ordering to which the simple concepts do not apply. Where there do exist regions in a polymer describable by such terms as crystalline, glassy, rubber-like, etc., it is still necessary in a complete description to consider both the morphological character internal to the phase and, on a larger scale, correlations between regions of the different co-existing phases. Under contract to the Nonmetallic Materials Laboratory, Directorate of Materials and Processes, the Mellon Institute has initiated research work on the morphology of polymeric materials. Recently, development of theories regarding amorphous-crystalline relationships of polymeric materials have made possible fruitful investment in this research area. Mellon Institute's Dr. T. G. Fox and his co-workers are highly qualified to conduct research in this field and have available modern instrumentation and techniques for examining the problem. Complementary studies are also being conducted within the Nonmetallic Materials Laboratory in-house research program offering a cross-stimulation of ideas between the two groups involved. In addition to the obvious importance of such studies to the basic science, an understanding of the morphological attributes of high polymeric materials will greatly enhance their application to Air Force requirements. These requirements exist in such areas as plastics, fibers, elastomers, sealants, adhesives, and coatings.

EDITOR'S NOTE: WHILE AIR FORCE SYSTEMS COMMAND'S PRIMARY INTERESTS ARE NOT IN BASIC RESEARCH, THE ABOVE PROJECT IS BEING CONDUCTED BY AERONAUTICAL SYSTEMS DIVISION OF AFSC.

TO OUR READERS

The continuing goal of the "OAR RESEARCH REVIEW" is an attempt to satisfy the information needs of both the scientist and the nonscientist decision maker, since we feel each is of importance.

It is inevitable that many decisions concerning basic research, from the budget that supports it to the manner in which it is fed into applied research and development activities, are made by people who are not scientists.

We believe that it is imperative that these people be informed about research in progress, and understand something of its potentialities. It is equally imperative that the scientist be kept up-to-date on research projects occurring within his areas of interest. Each time this publication prevents needless duplication of effort by informing a research scientist of new knowledge discovered, it will have achieved an important contribution to the conservation of the Free World's scientific resources.

Those of you among our readers who feel a need for further information about a topic covered in any issue are urged to contact the author or originating laboratory direct. Addresses for use on such occasions are shown on inside back cover of this issue.

Constructive criticism and suggestions for improvement will be most welcome, and should be directed to this headquarters, ATTN: RREI.

Daniel E. Hooks

DANIEL E. HOOKS
Major General, USAF
Commander

DIHWITIHODIN...
or ash me your questions

LEONARD SPIALTER, Chemistry Research Laboratory, (ARL)

"Do I Have What I Think I Have Or Do I Not?" is the first question asked by the chemist after he has run a synthetical reaction designed to prepare a certain molecule. The answer is sought by subsequent analytical methods. In organometallic compounds the initial question usually revolves about whether the product or products isolated even contain the desired metal atom chemically bound. The reaction desired may not have gone or else the subsequent processing may have eliminated it from the final molecule. In these latter cases a negative answer can eliminate erroneous assumptions and needless experimentation.

This general problem of quickly recognizing the presence of bound metallic or metalloidal elements is a frequent one plaguing the organosilicon research program in the Chemistry Research Laboratory of the Aeronautical Research Laboratories. Tne usual analytical methods, such as spectroscopy or quantitative microanalysis are good and necessary back-stop procedures, but suffer from slowness and may not be most convenient for a complex molecule.

The simplest answer to the problem seemed a priori to lie in some combustion and ashing procedure. However, the obvious and conventional methods for producing ash, such as the burning of samples held on spatulas, wire loops, crucibles, etc., were not only wasteful of material but usually did not work successfully. Combustion of a sample at the open end of a capillary tube succeeded in giving a visible ash in the case of highly and moderately volatile alkylsilanes but failed in all cases with aromatic compounds. These latter produced carbonaceous deposits which were difficult to oxidize and which very readily fused into the flass with no sign of the expected ash.

Now, Drs. Leonard Spialter and Manuel Ballester (on one year leave from the University of Barcelona, Spain) of the Organic Group of the Chemistry Research Laboratory have found a very rapid, unequivocal, and simple procedure which on a sample of less than one milligram (about one thirty-thousandths of an ounce) will not

only indicate the presence of either silicon, germanium, tin or lead in a molecule but will also identify the metal-- in less than two minutes.

The Spialter-Ballester metnod makes use of the concept that the combustion of organometallic compounds should give a residue of metal oxide ash. However, conventional burning procedures use much material and do not always leave a residual deposit in the case of the volatile and /or thermally stable organometallics. Study of various ashing techniques and analysis of the observations finally led Spialter and Ballester to their simple, yet effective design and ashing technique.

The apparatus consists of a nichrome or platinum wire about 5 cm. long which has a small hook at one end, bears a thin-walled capillary glass sleeve, and is inserted into a holder at its other end. Each component of the apparatus is crucial and indispensable. The sample of unknown substance is initially placed in the wire hook. The ashing is performed in two steps involving, first, burning, and, the, oxidation in a relatively cool oxidizing flame of a properly adjusted Bunsen burner.

With the proper technique the operator, in positive cases, observes formation of an ash on the glass capillary near the hook. From the nature of the deposit, the metal atom can be identified: silicon gives a grey-white deposit which is heat stable; germanium gives a grey-white deposit which easily fuses into the glass and disappears; tin yields a stable bright white powder; while lead leaves a yellow residue which very readily melts into the glass. The nature of the flame in the initial burning operation, whether self-sustaining or not, and the formation or absence of a preliminary carbon deposit have been found to be systematically related to the structure of chemical sample. These observations can be used to categorize the unknown as to presence of aromatic substituents, ease of thermal decomposition, relative volatility, size of alkylsubstituents, etc.

This method has been applied to more than 40 organosilicon compounds of all structure types as well as to several organic derivatives of germanium, tin and lead with complete clear-cut success. Examination of the experimental data show that self-sustaining flames during the initial burning period of the test are associated with the

more volatile compounds, such as the alkylated simple molecules, or with those like the tetracyclohexylsilane and tetrathienylsilane which, though relatively non-volatile, readily decompose at the flame temperature to give volatile combustible products. The highly arylated molecules and those with high boiling points, appreciable molecular weight and good thermal stability, such as silicone oil and grease, required continuous heat input during the flaming operation.

Carbonaceous deposits formed during the intermediate stages of the ashing procedure were found to be associated with the presence of aromatic groups in the molecule. Generally, compounds not possessing such groups give clean ash immediately after the preliminary combustion. However, no difficulty was found in burning away the carbonaceous deposits to leave unequivocally positive white or yellow (depending on the metallic atom present) residues on the thin-walled capillary tube near the wire hook.

It appears probable that the described procedure is applicable also to other compounds containing elements whose oxides are relatively non-volatile and do not react with the capillary material at the temperatures used. The chemical identity of the ash deposit from the sample can, of course, be readily verified by standard qualitative analytical tests such as X-ray diffraction or by suitable treatment for the appropriate spot tests.

Although samples of about one milligram have been used, addition of such refinements as a smaller combustion assembly, a microburner and examination under a microscope undoubtedly would permit extension of the method to even more minute quantities.

The Spialter-Ballester ashing procedure has greatly facilitated interpretation and preliminary identification of reaction products in the organometallic research program of the Aeronautical Research Laboratories. Its routine use has also increased the efficiency of operations involving the analysis and separation of mixtures, including recrystallization and both liquid and vapor phase chromatography. For workers in organometallic chemistry, this simple test may prove as handy a technique as is the well-known Beilstein test for those investigating halogen-containing compounds.

The details of the Spialter-Ballester method, its apparatus and results, have been described in a paper submitted for publication in the journal Analytical Chemistry.

Vibrational Distribution Functions for Cubic Lattices

DONN G. SHANKLAND, General Physics Research Branch, (ARP) ARL

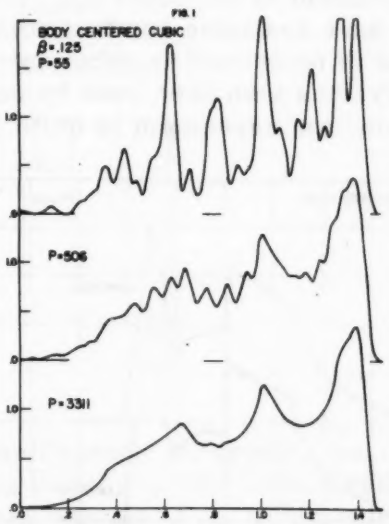
The vibrational distribution functions for Simple, Body-Centered, and Face-Centered Cubic lattices have been computed for a wide variety of ratios of nearest to next-nearest neighbor interactions. The Simple Cubic calculations completely verify previous calculations. As expected, the BCC distribution functions are at variance with previous results. However, discrepancies between our BCC results and a topological analysis indicate that the topological analysis must be used with care, as exceptional cases occur. The FCC calculation agrees with that of Leighton, but again shows that the topological analysis can be highly misleading. Specific heats obtained from these distribution functions, as anticipated, do not depend critically on the details of the distribution function.

The problem of calculating the vibrational distribution function, used in specific heat calculations and calculations of scattering of neutrons and x-rays, has been with us since 1912, when Born & Von Karman suggested that an accurate calculation of the density of vibrational states should enable one to obtain better agreement with specific heats of solids than had been possible previously. However serious attempts to actually carry out such a program date from the numerical work of Blackman in 1935, and have been made only sporadically since that time. The principal reason for this is the enormous amount of labor involved in such a direct calculation, involving the diagonalization of hundreds and even thousands of secular determinants, in order to obtain a representative histogram of the distribution of the eigenvalues. Other methods for carrying out the calculation, based on analytic or approximate methods have also been advanced in order to lighten the burden. However, for a complicated lattice, no method other than the direct numerical one is at present available, and so when a knowledge of the specific heat and vibrational absorption spectrum of a complicated lattice was needed in our laboratory, we undertook such a numerical calculation.

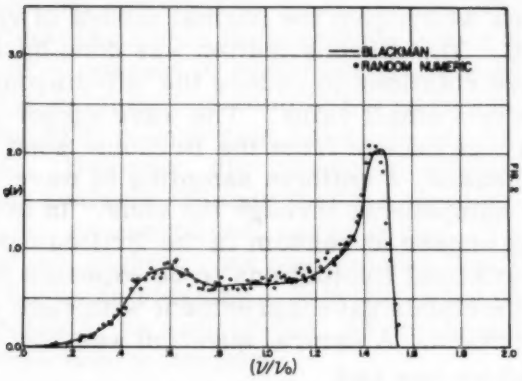
In order to check on the program used, we recalculated the spectra for the various cubic lattices, which are already available in the literature. The results are, we think, of sufficient interest in their own right that we present them here. Briefly, these results are that the direct numerical calculations which have been done in the past are, essentially, correct, as is the moment method of

Montroll, but that the other methods used for estimating the distribution functions, those of Houston and Rosenstock, are essentially incorrect, and must be used with extreme care, if at all.

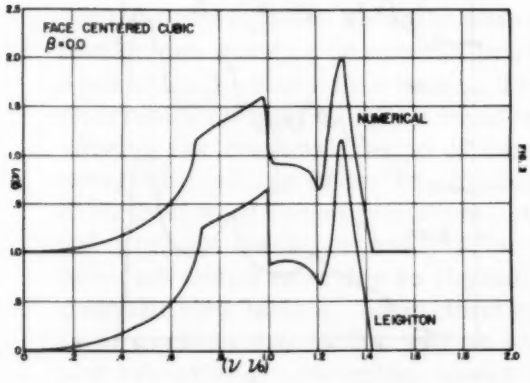
The computations presented here were done on an IBM 7090, and are simply histograms of the distribution of eigenvalues of the secular determinants which give the normal modes of vibration of the lattices involved. The diagonalization was done by Jacobi's method of successive rotations to reduce the off-diagonal elements of the determinants to a small value. The wave vector of the particular determinant was chosen from the Brillouin zone in one of two ways. In some cases, a uniform sampling of wave vectors was made, stepping the components through the zone. In other cases, the wave vector was chosen at random in the Brillouin zone, and the results show the statistical fluctuations to be expected of a random sampling. The two methods gave agreement with each other, within the errors to be expected. A natural question was how many points in the reciprocal lattice one had to take in order to get a representative distribution function. Figure 1 shows the sort of results achieved, using the indicated number of points. As you can see, one needs about 10^5 points in the reciprocal lattice to get a decent function. However, this is also a function of the number of channels in the histogram, and also of the type of lattice and the force constants involved. With certain lattices, such as the simple cubic, with no second-neighbor interaction, one obtains very poor results. It is in these cases that the random sampling technique was used. The data even with many cases shows fluctuations which are discouraging, considering that one believes that there really is a "function" representing the density of states. Accordingly, the data was smoothed for most applications, the smoothing technique being, usually, the replacement of the value in a channel by the average of the three channels nearest the points. Averaging by fives was also used, and sometimes the process was re-

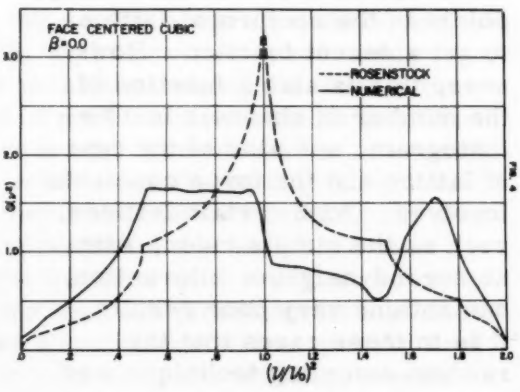


peated a second time. The first calculations were on the simple cubic lattice, for which extensive calculations have been done in the past by Blackman, using a direct numerical technique; and by Montroll, using his method of moments. Blackman's curve, together with the raw data from a statistical calculation, is shown in Figure 2. The



agreement is excellent and credits the efforts of Blackman, who did not have available any fast computers or similar timesavers. The case of no second neighbor interaction, which can be solved analytically, has also been done by using the random sampling method. Again, the agreement is quite good.

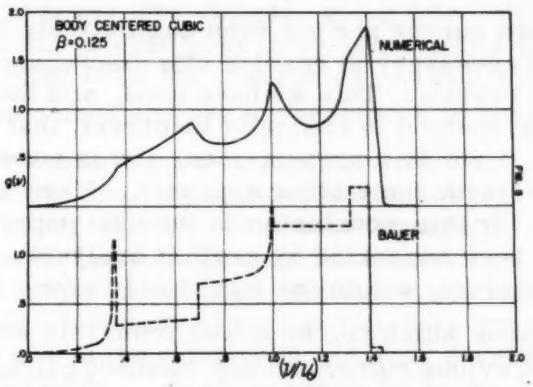




The calculations on the face centered cubic lattice, carried out by Leighton, using volume measurements on models of the constant-frequency surfaces, are shown with the results of my calculations in Figure 3. The agreement is again quite good, especially considering the labor involved in carving and measuring the models. Figure 4 shows, however, the prediction of Rosenstock for the face-centered lattice, together with the results of the numerical program.

These curves are the distribution of the squares of the eigenvalues, as this is the quantity which the topological approach most easily considers. Some of the features of the topological analysis are reproduced, but the overall agreement is far from encouraging, there being discrepancies, for instance, for the value $(V/Vo)^2=1$, the curve of Rosenstock has a nearly symmetric infinite peak, whereas the numerical curve shows a finite discontinuity. In the case of the face-centered lattice, there is some experimental data which results from measurements of x-ray scattering on aluminum. The curves are vaguely similar, but the agreement is not good.

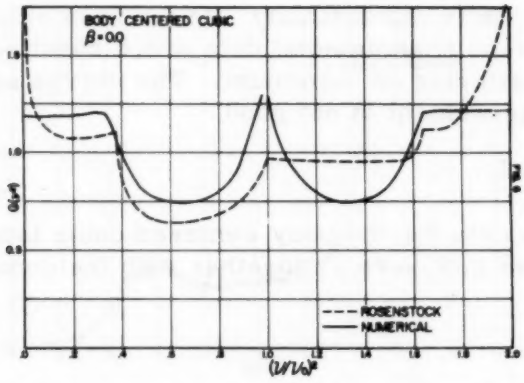
Finally, the data for the body centered cubic lattice, as obtained by Bauer, is shown in Figure 5, together with the numerical results



of my program. The data of Bauer is sufficiently uncertain, due to the approximations involved in obtaining them, that one cannot really expect better agreement. Bauer himself indicated this in his original article, and his results were certainly the best that could be obtained at the time without excessive hand labor. The present data, then, should be regarded as an accurate calculation for the body-centered case. The calculations were done for several values of the interaction parameters, in the hopes that the specific heat curves could be improved thereby. However, because of the extreme insensitivity of the specific heat curve to the details of the spectrum and the approximations in treating the electronic contribution, the specific heat curve

is not materially improved.

The results of the approach of Rosenstock for the body-centered case are shown, together with the numerical data in Figure 6. Here again, the discrepancy between his approach and the numerical one is apparent. In fact, for the case of the no next-nearest neighbor



interaction, the two curves are not even qualitatively the same. Obviously, it was necessary to resolve this discrepancy before offering the numerical results. This we have done, and the conclusion is that the topological method is basically incorrect; that together with correct answers, it yields incorrect ones, and is not to be trusted, except as it agrees with some other approach. More will be said about the reasons for this conclusion in the next paper, but the behavior shown has been supported by explicit analysis, and is accordingly offered as correct, within the statistical errors involved.

The conclusions which can be drawn from this work are threefold:

First, the previous numerical and moment calculations have been supported and verified in all cases. Second, the approach of Houston using selected directions in the crystal is explicitly shown to be inadequate, even a simple direct calculation giving a much better representation of the actual situation. Third, the topological approach is shown to be incorrect, it yielding misleading data and outright incorrect behaviour of the curve, without warning. It does give one justification for drawing sharp edges and corners, where it predicts them and where the numerical data also seems to indicate them. By where it disagrees, it must be discounted until some other analytic approach is used to resolve the question. For any practical sort of application of the spectrum calculation, it seems that the numerical method, with the use of a fast computer, gives a more reliable result in a very reasonable time, and must be used for all but the simplest of cases.

ISOLATION

HARVEY E. SAVELY, Life Sciences Directorate, AFOSR

A topic of considerable research and technological interest is the effects of isolation for either brief or prolonged periods. Studies are being made on man and on his lower vertebrate relatives. An important aspect of this problem is the effect of isolation of young animals on the development of their behavior. Dr. Ronald Melzack, MIT, working on an AFOSR grant, has been interested in this problem. Three litters of beagles were divided at three weeks of age into a group of eight shut up in individual boxes, and a group of six which was given a normal happy puppyhood on a farm. He is now observing the differences in the behavior of these groups. His early results show that the puppies shut away for six months are strange animals indeed. Their deportment is infantile, erratic, bumbling, excited, and with an unusual disregard to pain. They will thrash about excitedly, banging their heads into objects, going into "whirling fits" on slight provocation, or even poke their noses into a flame, but without any sign of learning from the experience, or being disturbed by it. They ignore other dogs and are unresponsive to human petting.

When these animals are compared with their farm-raised litter mates in a psychological apparatus designed to test learning and discrimination, further differences become apparent. The restricted dogs take longer to learn to discriminate between a white and black card, and still longer to catch on when the significance of the cards is reversed. Tests of pattern recognition have not been completed so far because one of the farm dogs suddenly developed a profound change in "personality." In all respects he began to act like the restricted dogs, and even developed "superstitions," such as always turning around two times before responding to stimuli. The switch from the happy life on the farm to an MIT laboratory to live in a cage and to be put into the infernal testing boxes of psychologists was too much. We can sympathize with him.

Dr. Melzack is now preparing to mount permanent electrodes and temperature sensors into the brains of his animals and monitor the telemetered signals to find out more about the source of the abnormal behavior. Many theoretical questions about the development of behavior, learning, and pattern recognition will be examined by these and other psychological tests. These questions have general psychological significance and possible application to human problems arising from an environment of restricted sensory inputs.

a not-so-magic formula

B. H. SMITH, 1st Lt, USAF, Chemical Sciences Directorate, AFOSR

It is quite obvious that the formula is a primary and important piece of datum for the study of compounds, both new and known. There are, however, two types of formulae one may consider: Empirical formula and molecular formula. The EMPIRICAL FORMULA indicates the simple, relative proportions of different atoms in a molecule. The MOLECULAR FORMULA is that formula which describes a single molecular entity in terms of both the atomic proportions and the molecular weight. In many cases, organic compounds particularly, though the phenomenon extends into inorganic chemistry, the empirical and molecular formulae are not identical. For instance, formaldehyde, acetic acid, and glucose all have an empirical formula of CH_2O while their molecular formulae are CH_2O, $C_2H_4O_2$ and $C_6H_{12}O_6$, respectively.

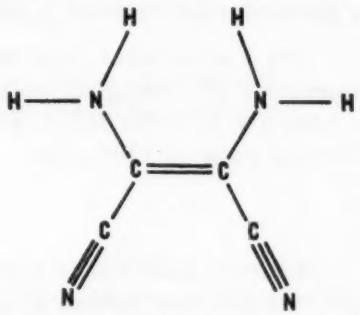
Further complicating the picture is the possibility of one compound exhibiting two different molecular formulae. Hydrogen cyanide is a case in point. Usually (i.e., under most laboratory conditions, and uses), it is simply HCN, empirical and molecular formulae being identical but, under certain conditions, it exists as a species whose formula is a multiple of the empirical state.

The exact number of the multiple has long been disputed by chemists. For years, the tetrameric form, $H_4C_4N_4$, was accepted. In 1959, Wadsten and Anderson claimed a dimeric form, $H_2C_2N_2$, to be the true state.

Now, just recently, Dr. William N. Lipscomb, of Harvard University, with the support of the AFOSR, has settled the controversy with what he feels is conclusive structural proof for the tetramer, diaminomaleonitrile. Other men interested in this problem had determined certain fundamental data about this solid, but it remained for Dr. Lipscomb to do a complete, unambiguous analysis.

Using standard, basic X-ray techniques, but with a novel mathematical modification, the Harvard group determined the true molecular

structure of this molecule (See Fig.). One indication of the magnitude of the problem is that about 900 individual X-ray reflections were considered in accurately determining the atomic positions, and thus the bond lengths and angles of the twelve atoms. Although perhaps not obvious, the carbon-nitrogen skeleton of the molecule is planar.



This determination is but one of an important series on unusual molecules being studied by Dr. Lipscomb and his group. The boranes, certain enzymes, naturally occurring alkaloids, and others are being investigated. An unclouded knowledge of how these molecures are constructed will inevitably result in a clear picture of why they behave as they do. Additionally, this will help to relate their behavior and properties to their structure. Value to Air Force researchers is obvious. Any advance in understanding structure-reactivity relationships results in more specific syntheses, uses, and understanding of the host of Air Force materials.

SENSITIVE RADIOMETER FOR PLASMA STUDY

Electromagnetic Radiation Laboratory (ERD, CRL)

The plasma sheath enveloping a hypersonic vehicle on reentry into the atmosphere generates radio noise. The study of this noise may furnish clues as to characteristics of the plasma sheath, and thus may suggest methods for obtaining more reliable communications with reentry vehicles.

To investigate the properties of plasma noise, AFCRL has designed a highly sensitive radiometer to be carried in test vehicles. The AFCRL radiometer is a miniature transistorized crystal video receiver. The radiometer is basically of the Dicke type, in which the noise generated by the plasma is compared to a reference noise source within the receiver.

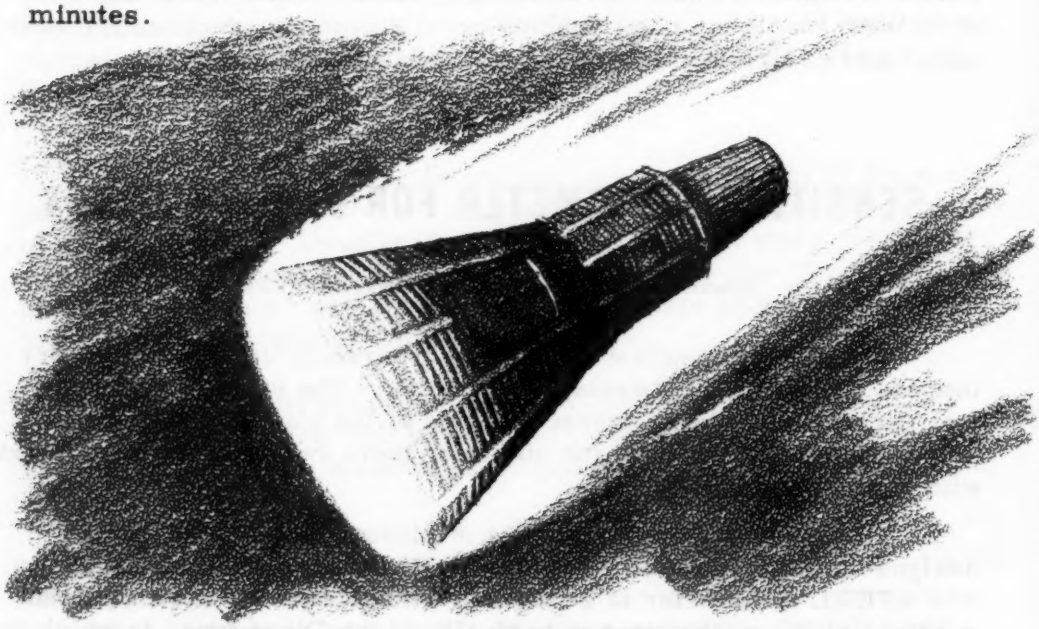
The comparison is accomplished by switching the input of the radiometer from the receiving antenna to the internal noise reference at a rapid rate. This procedure causes the incoming noise signal to

be modulated at the switching frequency. The modulated noise is then amplified in a narrow band amplifier. The output of the amplifier is fed to a coherent detector which produces a dc voltage at its output proportional to the difference in levels between the noise and the reference. This output is then converted to the proper form for transmission to a ground station over a telemetry link.

The radiometer was designed to be used over a wide range of frequencies by changing only the r.f. components. The first package will operate at 2000 Mcps with an input bandwidth of 200 Mcps and a switching rate of 1000 Cps.

* * * * *

A much-publicized aspect of the first manned Mercury orbital flight was the disruption of communications during the critical reentry phase. Communications to and from the vehicle were cut off for several minutes. During Dyna-Soar vehicle reentry, the pilot may be isolated from ground communications for a period up to thirty minutes.



The ionized gas layer -- the plasma sheath -- which severely attenuates radio signals to and from the reentering vehicle is one of the major unsolved space operational problems. Some 700 persons concerned with plasma sheath research focused their attention on this problem at a conference sponsored by AFCRL held in Boston this past April 10-12, 1962.

to our readers

Requests for further information, copies of detailed reports, etc. should be directed to the individual or laboratory of origin.

Addresses are as follows:

For reports originating within Air Force Cambridge Research Laboratories:

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
Laurence G. Hanscom Field
Bedford, Massachusetts

For reports originating within Aeronautical Research Laboratory:

AERONAUTICAL RESEARCH LABORATORIES
Wright-Patterson Air Force Base, Ohio

For reports originating within Air Force Office of Scientific Research:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Tempo D Building
4th and Independence Ave., S.W.
Washington 25, D.C.

RESEARCH REVIEW is published by the Office of Information (RREI), Office of Aerospace Research, USAF, Washington 25, D. C. The frequency of this publication will be determined solely on the basis of the availability of significant material to report. The objective is to make a positive contribution to the exchange of information about Air Force sponsored and conducted basic research activities.

GPO 929119